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Increased SO2 Removal with the Addition of Alkali Metals and Chromium to Calcium-Based Sorbents

Energy and Environmental Research Corp., Irvine, CA

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16. ABSTRACT

The paper discusses recent investigations that indicate that a small addition of certain chemical reagents can enhance or inhibit the ability of calcium sorbents to capture sulfur. (NOTE: The need to develop a low-cost retrofittable SOx control technology for existing non-NSPS boilers has caused renewed interest in the injection of calcium-based sorbents; however, the removal of SOx at a calcium/sulfur ratio of 2 has been limited to about 50%.) Initially, Cr2O3 was found to dramatically improve the sulfur capture of limestone. Chromium (e.g., Cr2O3) combined with calcium-based sorbents increased sulfur capture by a factor of 1.5-3 at conditions simulating a coal-fired boiler. Subsequently, alkali metal copounds (Li, Na, K) gave similar results. While small amounts of alkali metals enhanced sulfur capture by the CaO, they were also found to react with SO2 to form alkali metal sulfates. Some refractory oxides and clays typically found in coals were shown to reduce the effectiveness of additives which improve sulfur capture. While calcium utilization for the advanced sorbents has increased capture efficiencies with the use of promoters, the mechanisms of promotion have not been identified. This investigation studied mechanistic processes by which additives promote the ability of sorbents to capture SO2 in coal-fired boilers.

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Limestone	Pollution Control	13B	08G
Sulfur Oxides	Coal	Stationary Sources	07B	21D
Alkali Metals	Combustion			21B
Chromium	Boilers			13A
Sorbents				
Calcium Oxides			11G	

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INCREASED SO_x REMOVAL WITH THE ADDITION OF ALKALI METALS AND CHROMIUM TO CALCIUM-BASED SORBENTS

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Injection of calcium-based sorbents is currently being considered as a potential method of reducing SO_2 in existing coal-fired boilers. This study investigated the ability of small concentrations of additives to enhance sulfur capture with calcium-based sorbents. The interaction between the mineral ash (produced from coal combustion) and the sorbent-additive combination was also studied. Two furnace facilities and an X-ray diffractometer were used in the experimental study. The furnaces used included a 300 kW down-fired furnace capable of simulating time and temperature profiles for a variety of boilers, and a bench-scale 18 kW drop-tube furnace.

Addition of known promoters with sorbents has effectively increased sulfur capture. Both alkali metals and chromium react with calcium to increase the accessibility of CaO sites by particle fragmentation, creation of large pores, and the presence of a liquid phase. In general, the chromium eliminated by ash interaction was small, while the ash effectively prevented a significant portion of sodium from contacting and reacting with the calcium sorbent.

Introduction

The need to develop a low-cost, retrofittable SO_x control technology for existing non-NSPS* boilers has caused renewed interest in the injection of calcium-based sorbents. However, the removal of SO_x at a calcium-to-sulfur ratio of 2 has been limited to about 50 percent. Recent investigations indicate that a small addition of certain chemical reagents can enhance or inhibit the ability of calcium sorbents to capture sulfur. Initially, Cr_2O_3 was found to dramatically improve the sulfur capture of limestone.[1] Chromium (e.g., Cr_2O_3) combined with calcium-based sorbents (Ca/Cr atomic ratio ~15) increased sulfur capture by a factor of 1.5–3 at conditions simulating a coal-fired boiler. Subsequently, alkali metal compounds (lithium, sodium, potassium) gave similar results.[2,3] While small amounts of alkali metals (e.g., Ca/Na atomic ratio ~15) enhanced sulfur capture by the calcium oxide, they were also found to react with SO_2 to form alkali metal sulfates. Some refractory oxides and clays typically found in coals were shown to reduce the effectiveness of additives which improve sulfur capture.[4]

While calcium utilization for the advanced sorbents has increased capture efficiencies with the use of promoters, the mechanisms of promotion have not been identified. This investigation studied mechanistic processes by which additives promote the ability of sorbents to capture SO_2 in coal fired boilers.

Experimental Facilities

Combustion Furnaces:

Sulfur capture under boiler conditions was determined using the 300 kW Boiler Simulator Furnace (BSF) illustrated in Fig. 1a. The furnace is designed to simulate the complete time/temperature profiles of a wide range of commercial boilers. The facility consists of two main sections: a refractory-lined vertical radiant tower 0.56 m in diameter, 5.8 m tall with multiple access ports, and a horizontal convective section in which heat is extracted to simulate convective tube passages.

*NSPS-New Source Performance Standards.

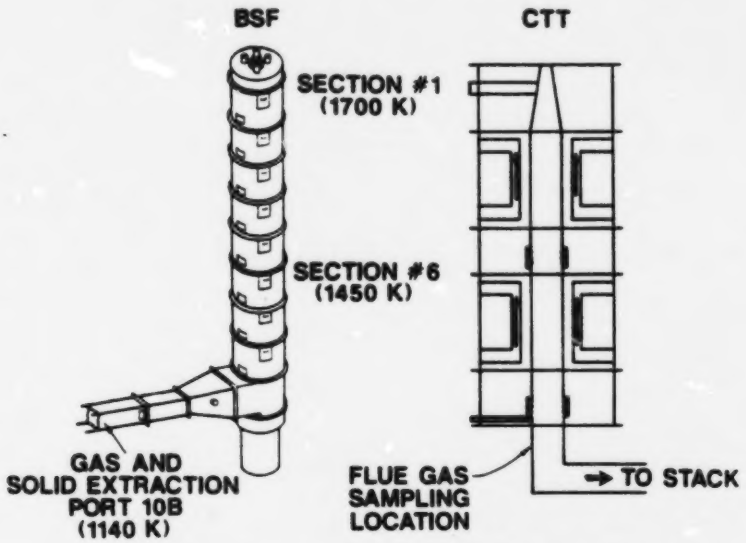

FIG. 1. Furnace schematics of BSF (left) and CTT (right).

The Control Temperature Tower Furnace (CTT) is used to provide temperature controlled reaction conditions. The schematic of the 18 kW CTT is presented in Fig. 1b. The quarl produces a stable flame with one-dimensional flow. Ports located along the axis of the reactor allow for variations, such as fuel, sorbent, and air injectors, and cooling coils, to be placed in the reactor. A variety of time/temperature profiles are obtained by firing one or both of the back-fired heating sections.

In both combustors, sulfur removal with calcium sorbents was monitored in natural gas and coal flames. For the natural gas studies, sulfur from coal was simulated by the injection of H_2S at the burner to produce approximately 2000 ppm SO_2. Calcium carbonate, and calcium hydroxide premixed with powdered promoters were used as sorbents in these studies. The calcium-based sorbents with promoters were fed from a calibrated, twin-screw volumetric feeder and injected near the burner or downstream to determine the influence of time/temperature history on sulfur capture efficiency.

Exhaust gas samples were withdrawn from the furnaces with a stainless steel, water-cooled probe and analyzed using standard continuous instrumentation for NO, CO, CO_2, and O_2. Samples for SO_2 analysis were drawn through a phase discrimination probe which separated reactive sorbent particles from the hot gas stream. The SO_2 samples were then passed through a heated sample line to a permeation dryer and a DuPont nondispersive ultraviolet SO_2 analyzer.

Solid sorbent samples for physical and chemical characterization were collected with a stainless steel, temperature-controlled probe followed immediately by a high temperature filter. At the conclusion of sampling, N_2 was used to reduce the sample filter temperature to ambient. The samples were carefully extracted and stored.

Dynamic X-Ray Diffractometer:

Isothermal experiments were done on a dynamic X-ray diffractometer to determine promoter and sorbent interactions under more controlled conditions. Typically, a bulk sorbent sample was placed on a heating strip which was in turn placed in an enclosed temperature-programmable hot stage where a simulated combustion gas (2000 ppm of SO_2, 6% O_2, 8% CO_2 in N_2) flowed over the sample. For data acquisition, the goniometer was used with digital control to measure predetermined diffraction angles. The data collected by the scintillation counter at each angle were recorded on hard discs as a function of time. At the end of an experimental run, the data were recalled and analyzed to obtain the rates of chemical species formation and destruction (e.g., $CaCO_3$, CaO, and $CaSO_4$).

At 1023 K, the calcination and sulfation processes are not sequential.[5] In order to eliminate the influence of the calcination process, limestone was precalcined at low temperatures to a specific surface area of 25 m^2/g. Vaporized Cr_2O_3, or $NaHCO_3$ was deposited on the precalcined limestone in a Varian vacuum evaporator to produce a fine

coating of the promoter with minimal physical damage to the sorbent.

Fuel and Sorbent Characterization:

Characterization of the coals used in this study is given in Table I. The coals were chosen based on their ash and total sulfur content. A "clean" coal was also tested. Table II summarizes the properties of the sorbents used in this study.

Results and Discussion

Promotion With Alkali Metals:

Alkali metals combined with limestone were effective for improving sulfur capture as shown in Fig. 2. Carbonate forms of the additive were premixed with limestone (Ca/X~15 atomic, X = Li, Na, or K) and injected into the CTT at 1450 K. While there was some variation in reactivity between the alkali metal additives (i.e., K > Na > Li), sulfur capture with additives was up to 50 percent greater than sulfur removal using limestone alone. To understand the interaction between calcium-based sorbents and alkali metals, sodium was selected for more detailed experiments.

The influence of limestone with sodium on sulfur capture is summarized in Fig. 3. Open symbols represent the capture measured with limestone alone, and shaded symbols represent capture that resulted from sodium-promoted sorbent (Ca/Na = 14.8 atomic). For injection temperatures of 1700 K and 1450 K, the increase in sulfur capture with promoted limestone was significant with sulfur capture at the high temperature equivalent to capture at the lower temperature. This result suggests that, at the higher temperature, promotion effects counterbalance the detrimental impact of thermal sintering. Sodium injected alone at 1700 K and 2000 ppm SO_2, reacts with sulfur to produce sodium sulfate. However, the overall increase in sulfur capture with the promoted sorbent is greater than can be explained with the formation of sodium sulfate only. The shaded areas shown in Fig. 3 represent

TABLE I
Fuel properties

Analysis (WT %)	Natural Gas	Indiana No. 3	Illinois No. 6	Lower Kittanning	Kentucky No. 11	"Cleaned" L. Kittanning
Proximate (as received)						
H_2O	—	5.07	15.77	11.23	28.09	12.29
Volatile Matter	100.00	30.24	35.44	15.27	19.37	17.45
Fixed Carbon	—	55.35	40.39	51.44	24.13	65.16
Ash	—	9.34	8.38	22.05	30.51	5.10
Ultimate						
H_2O	—	5.07	15.79	11.23	28.09	12.25
C	72.15	72.16	70.71	65.93	42.94	84.71
H	23.04	4.71	4.86	3.59	3.03	4.45
N	1.94	1.32	1.12	1.17	0.88	1.69
S	—	1.06	3.94	1.40	4.32	0.77
Cl	—	—	0.12	0.05	—	0.10
O	0.59	10.87	9.30	3.07	6.39	2.53
Ash	—	9.88	9.95	24.84	42.43	5.81
HHV(kW/kg)	14.67	8.10	9.12	7.44	5.01	9.57
Ash						
SiO		58.63	26.74	56.29	50.39	48.29
Al_2O_3		23.56	16.56	26.84	18.16	29.95
Fe_2O_3		10.26	18.33	8.38	12.99	12.58
CaO		0.95	6.21	0.65	5.02	2.03
MgO		0.36	0.85	0.67	1.14	0.56
K_2O		1.49	2.12	2.54	3.42	1.46
Na_2O		0.22	1.55	0.27	0.49	0.28
TiO_2		0.99	0.85	0.94	1.35	1.85
P_2O_5		0.47	0.18	0.16	1.65	0.29

TABLE II
Sorbent properties

Analysis	Vicron Limestone	Longview Calcium Hydrate	D3002 Dolomite	Genstar Pressure Hydrated Dolomite
Physical:				
BET SA (m^2/g)	2.0	16.1	—	—
Density (g/cm^3)	2.7	2.3	2.9	2.3
Median Size (μm)	9.8	3.9	11.8	1.4
Chemical: (Wt. %)				
Ca	39.20	48.80	24.80	30.30
Mg	0.33	1.21	11.30	16.00
Na	0.01	0.01	0.01	—
Si	0.09	0.30	0.16	0.13
Al	0.02	0.15	0.04	0.26
Fe	0.06	0.14	0.09	0.07
S	0.01	0.02	—	—
K	0.01	0.03	0.01	0.07

expected capture enhancement if all sodium reacts to form sodium sulfate.

Surface concentration of sodium on fired limestone changed the sorbent's morphology. High-resolution photography indicates that, as the sodium concentration on the sorbent surface increased, there was a reduction in the observed particle size and production of large cracks on the particle surface. Measured BET surface areas of sodium-promoted sorbents from this work and others[2] showed decreases relative to the unpromoted sorbent when injected under similar conditions. While this appears to contradict the increase in cracks observed on the surface of the promoted sorbent, it does not. The presence of sodium in the CaO matrix is believed to induce chemical sintering which reduces the smaller pores that are responsible for the majority of the measured surface area. The cracks and extent of fragmentation are believed to be caused by differences in local sintering rates between the sodium enriched and unpromoted CaO. These relatively large cracks increase the accessibility of SO_2 to reach interior reactive CaO sites. While additional large cracks produce small increases in surface area, they are not sufficient to counter the loss of surface from the reduction of smaller pores through sintering. Therefore, a net reduction in specific surface area is observed. (These morphological changes do not depend on the presence of SO_2.)

To identify the interaction of sodium with CaO, sodium-coated CaO particles were placed in the dynamic X-ray diffractometer under a simulated combustion gas at 1023 K. Results (Fig. 4) show that sodium promotion of CaO increased the overall kinetic rate for sulfation and the ultimate sulfur capture. Extracted solid samples were examined under a scanning electron microscope (SEM). The promoted CaO showed a reduced particle size and the formation of a liquid phase. Energy dispersive spectroscopy (EDS) analysis indicates that better sulfur capture coincides with the presence of the liquid phase.

A variety of calcium-based sorbents premixed with sodium bicarbonate were evaluated in the BSF to determine the influence of sorbent type on promoter performance. Four sorbents were examined: Vicron limestone, Longview calcium hydrate, D3002 dolomite, and Genstar pressure hydrated dolomite. Results are summarized in Fig. 5 for sorbent injection at 1450 K. The capture by limestone increased by 80 percent in the presence of sodium, while the promoted calcium hydrate and dolomite showed an increase of 25–50 percent. Sodium enhances fragmentation and macropore development through crack formation by the mechanism of chemical induced sintering. In general, hydrates already contain relatively small particles with an extensive macropore structure; therefore, sodium is less effective. In the case of D3002 dolomite (a Ca/Mg atomic ~1), the reason for not producing a greater enhancement is the presence of magnesium. Magnesium, at the conditions tested, produces an instability in the particle structure be-

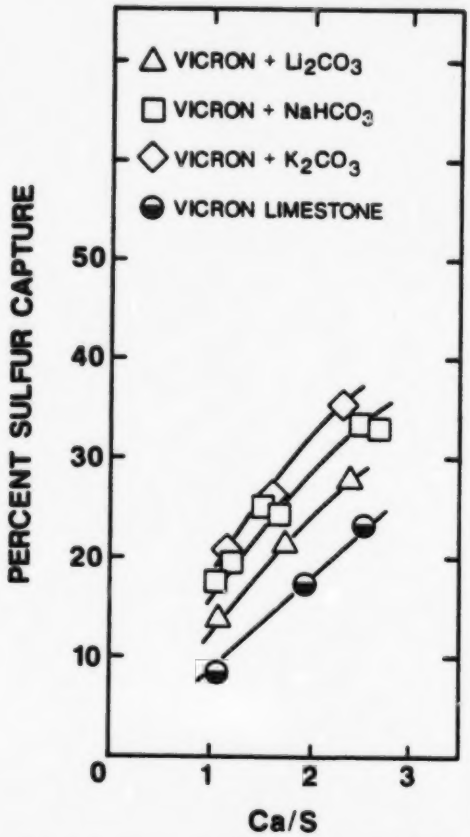

FIG. 2. Summary of sulfur capture with alkali metals. (Reactor-CTT; Fuel-Natural Gas/H_2S; Temperature-1450 K).

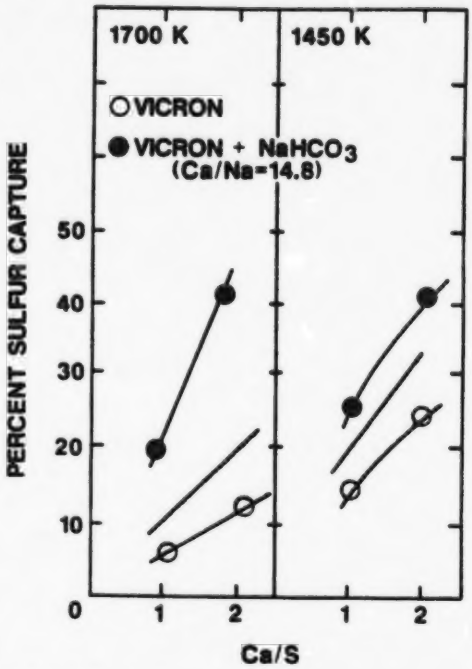

FIG. 3. Comparison in sulfur capture between fired Vicron limestone with and without $NaHCO_3$ present at two different temperatures (Reactor-BSF; Fuel-Natural Gas/H_2S).

cause of different sintering rates between MgO and CaO.[6] A relatively extensive pore (crack) network in fragmented particles is produced early in the calcination process which allows easy access to interior CaO sites.

In general, the sodium compounds tested readily vaporize under combustion temperatures. The sodium reacts with the CaO matrix to induce particle fragmentation and large cracks, thereby increasing the number of calcium oxide sites that are readily available. In addition, a sufficient concentration of sodium impregnated in calcium oxide produces a liquid mixture that is highly reactive. Differences in promotion between the various alkali metals are believed to be related to the cationic radii. The larger the cationic radii (e.g., $r_{K^+} > r_{Na^+} > r_{Li^+}$) penetrating the CaO matrix, the more extensive is the local crystal instability resulting in the production of smaller particles and a larger number of macropores.

Promotion With Chromium:

Figure 6 illustrates the influence of Cr_2O_3 addition to limestone and is indicative of results with

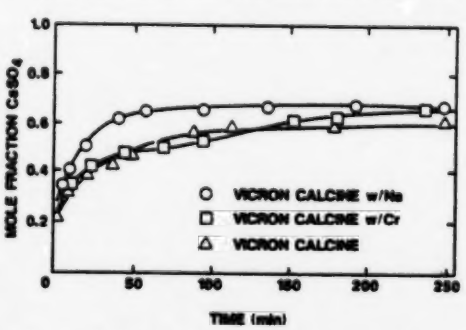

FIG. 4. Sulfation of evaporatively doped limestone (Reactor-DXRD; Temperature-1023 K; Simulation Gas-2000 ppm of SO_2, 6% O_2, and 8% CO_2 in N_2).

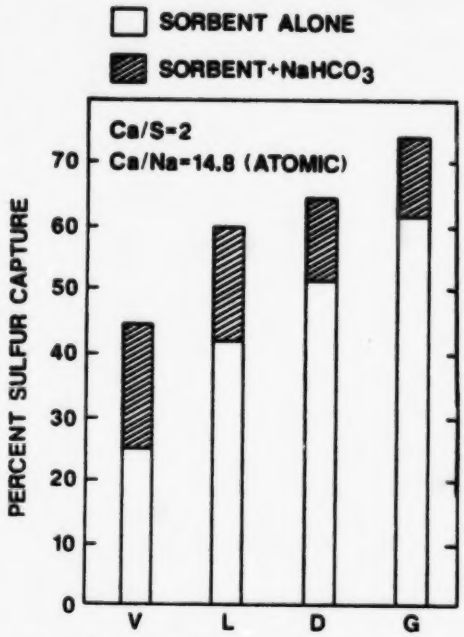

FIG. 5. Sulfur capture of sodium bicarbonate premixed with a variety of calcium-based sorbents (Reactor-BSF; Fuel-Natural Gas/H_2S; Temperature-1450 K; Sorbents-Vicron Limestone (V), Longview Calcium Hydrate (L), Dolomite D3002 (D), and Genstar Pressure Hydrated Dolomite (G)).

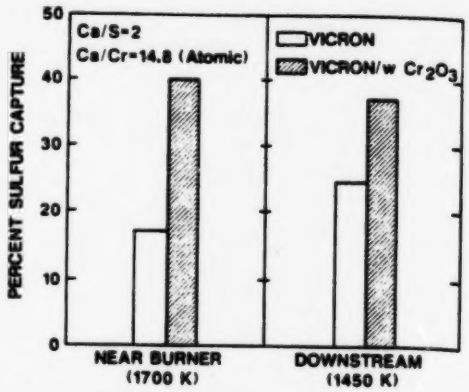

FIG. 6. Comparison in sulfur capture between fired Vicron limestone with and without Cr_2O_3 present at two different temperatures. (Reactor-BSF; Fuel-Natural Gas/H_2S).

other calcium-based sorbents. The open bars represent the capture measured with limestone alone, and the shaded bars indicate the increase in capture that resulted from a 5 weight percent chromium addition. At 1700 K and 1450 K, the increases in sulfur capture by the chromium-promoted limstone were significant with the higher temperature producing the larger enhancement. The absolute sulfur capture for high temperature injection was equivalent to the capture at the lower temperature. Progressively increasing the bulk concentration of chromium to 3 percent by weight increased sulfur removal, but capture efficiency declined with additions above 3 percent.

Injecting Cr_2O_3 without limestone at 1700 K and 2000 ppm SO_2 demonstrated that Cr_2O_3 did not react to form chromium sulfate. The experimental results confirmed thermodynamic calculations which suggest that chromium sulfates are not stable under the conditions tested.

Analyses were performed with a scanning electron microscope on extracted solids to identify changes in morphology of the sorbent with chromium. A distinct difference in the overall shape of the particles was observed. Fired limestone is rough, angular and contains a significant number of large pores; in contrast, the limestone with Cr_2O_3 appears smooth and more spherical in shape with the number of pores observed being severely reduced. Specific surface areas of the two solids were 12 m^2/g for limestone and 4 m^2/g for limestone with 5 percent by weight Cr_2O_3, supporting the SEM observations. Formation of spherical particles indicates the presence of a liquid phase. The melting temperatures of CaO and Cr_2O_3 are 2890 K and 2539 K, respectively. However, when combined, the mixture forms a low melting eutectic at 1273 K.[7] Both injection temperatures were above the theoretical temperature needed to produce a liquid phase. The presence of a liquid phase increased the diffusion of sulfur species to reactive calcium oxide sites, which would have been inaccessible in the solid phase.

In general, the observed particle sizes of the fired limestone with chromium were smaller than limestone fired alone. Extensive particle fragmentation is believed to be caused by chemically induced sintering. Spalling of an enriched chromium-calcium solid mixture creates new reactive surfaces for sulfur capture. In general, the reduction of particle size would increase calcium utilization by reducing the length of diffusion paths used by SO_2. Sulfated limestone/Cr_2O_3 solids analyzed for elemental distribution by EDS showed high chromium concentration associated with molten particles and high sulfur capture. The higher the concentration of chromium present, the more complete the transformation from a rough particle to a spherical particle.

While the chromium must be present in suffi-

cient quantities and in intimate contact with the calcium to effectively increase capture, the sulfur capture follows closely the amount of calcium present. A line-scan from a microprobe of sulfated limestone particles indicates that sulfur content traced the relative changes in calcium. Once a sufficient amount of chromium was present for enhancement, further chromium did not increase sulfur capture. X-ray diffractometry of solids indicates the formation of $CaSO_4$, $CaCrO_4$, CrO_3, and Cr_2O_3 in agreement with those specified in the phase diagram. This observation supports the results from gas-phase data which indicate no direct reaction to form chromium sulfates.

At lower injection temperatures, chromium distribution on the sorbent and subsequent penetration into the CaO matrix were reduced, as indicated by the limited $CaCrO_4$ seen in the diffraction analyses. While much of the solid results discussed thus far was based on the burner injection of limestone with Cr_2O_3, extracted solids from downstream injection tests reflected similar but less extensive changes. The samples contained some spheres, but also a large number of rough angular particles with only localized patches of chromium. Figure 6 indicates that chromium produced a smaller relative enhancement at lower temperatures. As noted above, chromium must be in intimate contact with calcium to provide a large enhancement. Therefore, a poor distribution of chromium at the lower temperature would yield a small enhancement.

Enhancement with Cr_2O_3 might have been due to the formation of SO_3, which is more reactive than SO_2 with CaO. While Cr_2O_3 is known to catalyze the conversion of SO_2 to SO_3, its effectiveness is inverse to temperature,[8] for temperatures 1475–1145 K, the SO_3 conversion from SO_2 is reduced to less than 10 percent. Distinguishing the relative importance of physical changes in the sorbent from chemical catalysis mechanisms is difficult under the thermal conditions typically used for sorbent evaluation. To avoid producing significant physical changes in the sorbent and to enhance the local catalytic conversion of SO_2 to SO_3 from 10 to 50 percent, the temperature was reduced to 1023 K. The reduction in experimental temperature reduced the kinetic rate for sulfation which allowed the chemical species produced (or eliminated) to be tracked as a function of time. The temperature, 1023 K, was determined to be above the temperature needed to ensure the formation of calcium sulfate rather than calcium sulfite or sulfide.

An EPA investigation[2] to determine the impact of Cr_2O_3 as an SO_2/SO_3 catalyst used Cr_2O_3 powder placed above calcium oxide, but physically separated from it in a differential reactor. An SO_2 gas at 1373 K flowed first through the Cr_2O_3 layer to produce SO_3 for reaction with the calcium oxide layer. The results showed no increase in sulfur capture. It was found in the present study that chromium must be in intimate contact with the sorbent to potentially be effective in producing additional sulfur capture. The dynamic X-ray diffractometer (DXRD) was used to determine the importance of precontacted chromium as an SO_2/SO_3 catalyst. Cr_2O_3 was evaporated on precalcined limestone to ensure intimate contact with the sorbent and reacted isothermally under a simulated combustion gas containing 2000 ppm SO_2. Results provided (in Fig. 4), for short times of 1 to 25 minutes, indicate no significant difference in overall reaction rate or ultimate sulfur capture. If the chromium operated as an SO_2/SO_3 catalyst, the initial rate of sulfation would have been higher. Capture performance of promoted limestone between times of 25 and 75 minutes yielded calcium utilizations lower than the unpromoted CaO which suggests that chromium physically blocked potential CaO sites. At 75 to 200 minutes, an increase in capture performance with the promoted limestone is believed to be caused by chromium penetrating the CaO crystal matrix ($CaCrO_4$ detected). Scanning electron microscopy with EDS analysis indicated that chromium-rich calcium sorbent effectively captured sulfur.

Chromium deposited without reaction on calcium-based sorbents did not measurably improve sulfur removal; this suggests that catalysis of SO_2 to SO_3 by Cr_2O_3 is not important in improving sulfur capture. It is clear that chromium penetrates the calcium oxide crystal structure, altering the sorbent physically. Accessibility to calcium oxide sites is increased by the reduction of effective particle size, the production macropores, and the formation of a liquid/solid mixture at the surface which substantially increases product-layer diffusion.

Reduction of Promoter Impact:

Coals were fired in the BSF to determine the influence of the chemistry of mineral ash on sulfur capture. Calcium carbonates and calcium hydroxides were injected at the burner and downstream which correspond to temperatures of 1700 and 1450 K, respectively. Figure 7 shows that sulfur reduction is independent of fuel type. In general, the extent of vaporization of the refractory oxides from coal is less than 1 percent[9] which suggests that particle agglomeration is the important mechanism for sorbent and mineral ash contacting. Simple particle collision calculations show that the number of ash-sorbent collisions in 3 seconds (estimated time in boiler) is small.

While the presence of mineral ash did not significantly alter the performance of unpromoted calcium-based sorbents, similar tests with promoted sorbents showed a dramatic decrease in SO_2 capture during coal firing. $NaHCO_3$ powder premixed

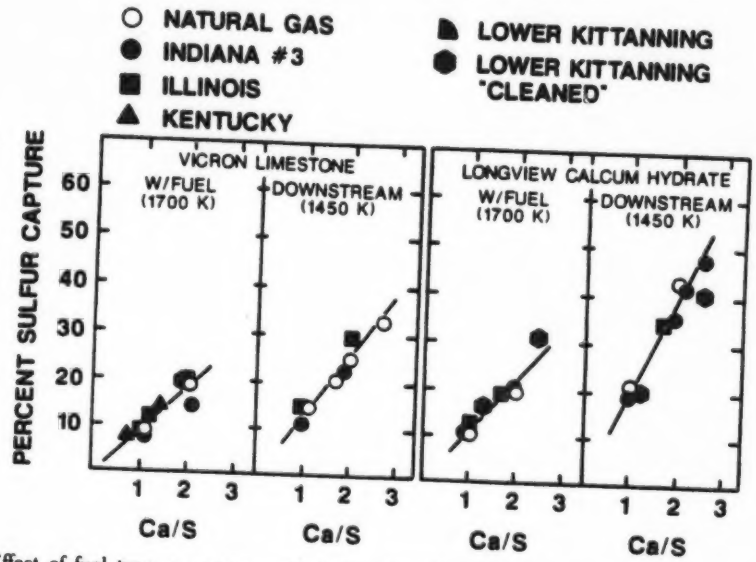

FIG. 7. Effect of fuel type on capture with Vicron limestone and Longview calcium hydrate (Reactor-BSF).

with calcium sorbents showed a significant reduction in sulfur capture in the presence of mineral ash. For sorbent injection at 1450 K, incremental sulfur capture due to sodium addition was reduced as the weight percent of mineral ash increased. A direct correlation of sulfur capture with mineral ash was not evident for chromium promotion. X-ray diffractograms indicate that the sodium reacted with the refractory oxides to form sodium silicates and thus effectively reduced the sodium available for reaction with the calcium sorbent. Sodium distribution based on EDS analysis confirms the presence of sodium on the mineral ash as well as on the sorbent.

In a combustion environment, ash and sorbent particles contain considerable surface area available for condensation of sodium. Calculations to determine the deposition characteristics of the sodium were performed using a numerical code, MAEROS.[10] This model describes the evolution of a distribution of aerosol particles influenced by coagulation, fragmentation, condensation, nucleation and deposition. Only physical phenomena were examined; other processes, such as chemical reactions which may enhance sodium removal, were not considered. In the calculations, an Indiana No. 3 coal is assumed burned at a stoichiometric ratio of 1.2 liberating an estimated 2.07 g-ash/m^3 into the boiler. The resulting ash distribution is assumed to be bimodal; with the submicron aerosol being characterized by a mean particle diameter of 0.2 micron, and the course ash represented by a mean diameter of 5 micron. Two sorbents were considered, Vicron limestone and Longview calcium hydrate. For simplicity, the particle size for fired sorbents followed a log-normal distribution which produced sorbent concentrations (in air) of 1.38 g/m^3 for limestone and 1.13 g/m^3 for calcium hydrate. The Ca/Na of 15 and Ca/S of 2 (atomic ratios) specified the amount of sodium and calcium associated with the sulfur. The condensing species is assumed to be Na_2SO_4 (condensation temperature ~1500 K).

Selected model results are summarized in Fig. 8 for fired limestone; here, the fraction of species greater than the given particle size is plotted against

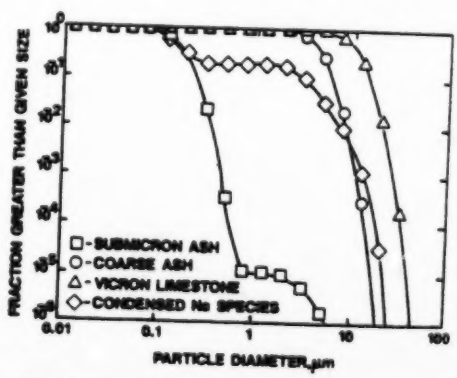

FIG. 8. Results from model calculations using the MAEROS code to predict sodium deposition.

particle diameter. Curves for the species (submicron ash, coarse ash, sodium, and sorbent) begin at 1.0 on the ordinate and trend toward zero as the particle diameter increases. Based on these results, approximately 20 percent of the sodium is associated with particles greater than 1 micron while the remainder falls in the sub-micron range. Therefore, coarse ash and sorbent particles competed for only a small percentage of the available sodium. Because calcium hydroxide has a smaller particle size than fired limestone (4 μm vs. 12 μm) and, therefore, a higher surface to mass ratio, the amount of sodium condensed on this sorbent is predicted from model calculations to be slightly higher.

Due to its lower volatility, the ability of chromium to promote sulfur capture was less affected than sodium in the presence of coal ash. The reduction of sodium was found to depend on the initial mineral matter content of the unfired coal, while the dependence of mineral ash on chromium was relatively weak.

Conclusions

Addition of known promoters with calcium-based sorbents has effectively increased sulfur capture. Both alkali-metals and chromium react with the calcium oxide to increase the accessibility to reactive sites by particle fragmentation, creation of large cracks (or pores), and the presence of a liquid phase.

In general the chromium eliminated by ash interactions was small, while the ash effectively prevented a significant portion of the sodium from contacting and reacting with the calcium sorbent. If the impact of the sodium promoter is to change the physical characteristics of the sorbent, as believed, process methods before injection may be implemented that allow interaction of the sodium without interference from the mineral ash.

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REFERENCES

1. Overmoe, B., Chen, S., Ho, L., Seeker, W., Heap, M., and Pershing, D.: "Boiler Simulator Studies on Sorbent Utilization for SO_2 Control." In Proceedings: First Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Vol. 1, p. 15-1, EPA-600/9-85-020a, NTIS PB85-232353, 1985.
2. Borgwardt, R., Bruce, K., and Blake, J.: "EPA Experimental Studies of the Mechanisms of Sulfur Capture by Limstone." In Proceedings: First Joint Symposium on Dry SO_2 and Simultaneous SO_2/NO_x Control Technologies, Vol. 1. p. 6-1, EPA-600/9-85-020a, NTIS PB85-232353, 1985.
3. Cole, J., Kramlich, J., Samuelsen, G., Seeker, W., Silcox, G.: "Fundamental Studies of Calcium-Based Sorbents for SO_2 Control from Coal-Fired Boilers: EPA-600/7-87-002 NTIS PB87-152500 1987.
4. Case, P., Ho, L., Clark, W., Kau, E., Pershing, D., Payne, R., Heap, M.: "Testing of Wall-Fired Furnaces to Reduce Emissions of NO, and SO_x: Volume 1." EPA-600/7-85-026a, NTIS PB85224632, 1985.
5. Borgwardt, R.: AIChE J. 31, 103 (1985).
6. Slaughter, D.: "Chemical and Physical Characteristics of Calcium Oxide for Enhanced SO_2 Reactivity." In: Formation and Control of Nitrogen and Sulfur Oxides in Suspension Coal Combustion, Ph.D. Dissertation, University of Utah, 1986.
7. Levin, E., Robbins, C., McMurdie, H.: Phase Diagrams for Ceramists, Vol. 1, p. 48, Amer. Cer. Soc., 1964.
8. Reid, W.: Chemistry of Coal Utilization 2nd Supp. Vol., Chap. 21, Wiley-Interscience, 1981.
9. Quann, R., Sarofim, A.: "Nineteenth Symposium (International) on Combustion." p. 1429, The Combustion Institute, 1983.
10. Gelbert, F.: "MAEROS Users Manual," Sandia National Laboratory Report No. SAND 80-0822, NUREG/CR-1391, 1982.

COMMENTS

T. Griffin, M.I.T., USA. Based on reduced additive effectiveness in the heated grid studies, have you made any conclusions regarding additive effectiveness on large-scale FBC conditions?

Have you planned (or performed) any experiments combining the Cr and Na additives? Is it possible that promotor properties of Cr and capture efficiencies of Na might combine in a way to give better performance than either additive alone?

Author's Reply. The use of chromium as an effective additive in a FBC will greatly depend on its dispersion and subsequent penetration into the CaO matrix. While the residence time in the combustor is considerably longer than in the pulverized coal combustor, the FBC operating temperature (~1200 K) is much lower which would reduce the rate of reaction between chromium and calcium. Thus, I would not expect chromium to be an effective additive under these conditions. It is believed that the alkali-metal (e.g., Na) additives would be more effective. The operating temperature in the FBC is sufficient for these more volatile additives to disperse and react with the calcium sorbent. Unfortunately, sodium species which are available for reaction with the sorbent may be reduced by condensation on other exposed surfaces or removed without reaction along with the exiting combustion gas.

The combined effects of sodium and chromium additives on calcium-based sorbents were not examined. At this time, it would be difficult to choose either of these additives (or combination) without addressing other concerns. For example, a method to selectively deposit sodium species on the sorbent is needed. This would reduce sodium's impact on deposition and corrosion processes at exposed surfaces along the gas flow path. While selective deposition is possible with chromium, there is a possibility of producing toxic chromium oxides in significant concentrations. (In addition, sources of chromium are limited.)

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S. Srinivasachar, PSI Technology Co., USA. How much of the sulfur capture would you attribute to vaporized chromium recondensing and then being sulfated?

Author's Reply. Chromium sulfate was not present in detectable amounts. This conclusion is based on X-ray diffraction studies in which samples of calcium-sorbents (with chromium) extracted from our test furnaces were analyzed for chromium species. In addition, selected samples underwent electron diffraction. Here again, diffraction patterns associated with chromium sulfate were not seen.

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